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Thermal studies of gel grown zinc tartrate spherulites

R M Dabhi and M J Joshi*

Physics Department, Saurashtra University,
Rajkot-360 005, Gujarat, India

E-mail : mshilp24@hotmail.com

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Abstract Zinc tartrate crystals have been grown by the gel method The effect of optically sensitive tartaric acids, *i e* dextro tartaric acid and levo tartaric acid, is studied. The crystals are found to have spherulitic nature. The thermal study is carried out by applying thermogravimetry The kinetic and thermodynamic parameters have been calculated from the thermogram for the dehydration process using Coats-Redfern, Horwitz-Metzger and Freeman-Carroll relations

Keywords : Spherulitic crystals, kinetic parameters, thermodynamics parameters, thermogravimetric analysis

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The effect of optically sensitive tartaric acids, *i.e.* levo tartaric acid and dextro tartaric acid, was reported for copper tartrate crystals [1]. In the present investigation, spherulitic crystals of zinc tartrate dihydrate have been grown by the gel technique using different optically sensitive tartaric acids, *i.e.* levo tartaric acid and dextro tartaric acid. The effect of optically sensitive tartaric acids on thermal decomposition is studied by thermogravimetry.

The crystallization apparatus employed were glass test tubes of 25 mm diameter and 140 mm length. The AR grade chemicals were used to grow the crystals. The gel was prepared from sodium metasilicate solution by acidification with levo tartaric acid as well as dextro tartaric acid. The specific gravity and pH were varied between 1.02 to 1.05 and 4.0 to 5.0, respectively. After setting the gel, the feed solution of 1M $ZnCl_2$ was poured without disturbing the gel surface. The nucleation was observed within 24 hours and spherulitic crystals were grown in a month having maximum diameter of 0.56 cm. Good quality crystals were grown for pH 4.5 and specific gravity 1.04. The following reaction is expected to occur during the process.

$$ZnCl_2.2H_2O + H_2C_4H_4O_6 \rightarrow ZnC_4H_4O_6.2H_2O + 2HCl$$

The thermogravimetric analysis (TGA) was carried out from room temperature to 800 °C at heating rate of 15 °C/min. in an atmosphere of air using NETZSCH Geratebau GmbH thermal analyzer.

Many investigators reported spherulitic morphology in the gel-grown crystals [2-4]. Also, a phenomenological theory of spherulitic crystallization was reported [5]. A spherulite, any crystalline body that is formed by the growth of radiating crystal fibers or concentric banding, is a polycrystalline aggregate and not a single crystal [6].

The infrared and thermal studies of calcium tartrate single crystals [7], neodymium tartrate crystals [8], iron tartrate spherulitic crystals [9] and copper tartrate crystals [11] have been conducted. Growth of zinc tartrate was reported by Henisch *et al* [10]. The characterizations of zinc tartrate crystals carried out by different techniques such as IR, TGA, XRD, dielectric measurements were reported by Lopez *et al* [11]. Templeton and

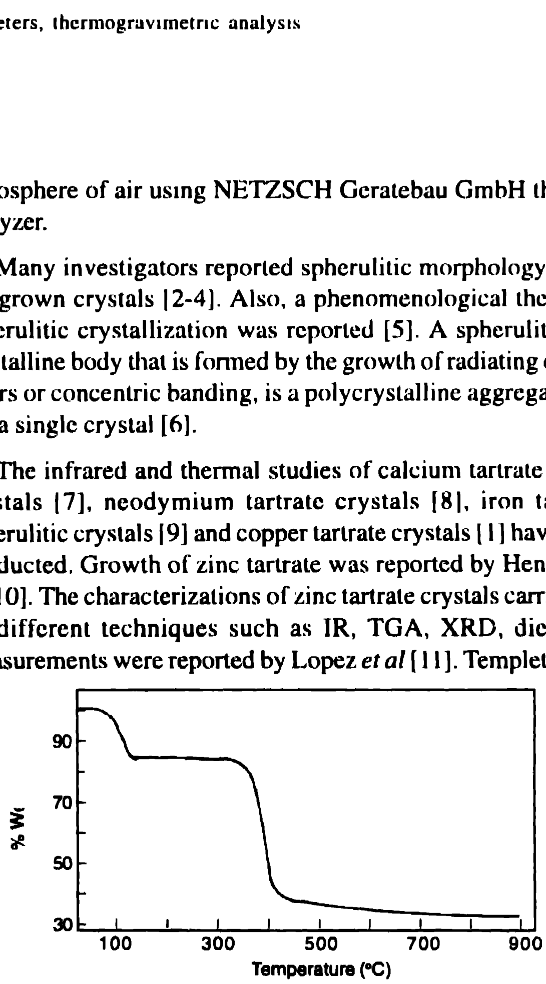

Figure 1. Thermogram of zinc levo tartrate.

* Corresponding Author

Templeton [12] have measured anomalous scattering terms for Zn^{2+} near the K-edge in diffraction experiment with zinc tartrate synchrotron radiation. The thermal properties can be studied with the help of thermogravimetric analysis (TGA). In the present investigation, the TGA was performed on the crystals collected from the bottom of the gel.

Figures 1 and 2 show the thermograms of zinc levo tartrate and zinc dextro tartrate crystals, respectively. As can be seen from Figure 1 that crystals decompose into anhydrous crystals at 120°C and then rapidly decompose into zinc dioxide at 450°C. Then crystals slowly decompose into zinc oxide at 800°C. Similar behavior is also observed for zinc dextro tartrate crystals. Table 1 shows theoretical and experimental values of weight in percent at different temperatures. From the calculations it was found that two water molecules are associated with zinc levo tartrate and zinc dextro tartrate crystals.

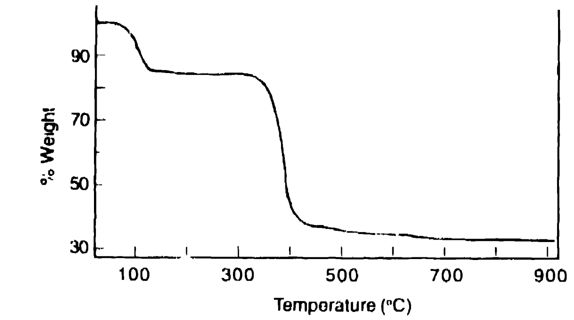

Figure 2. Thermogram of zinc dextro tartrate

Table 1. The type of decomposition products of zinc levo tartrate and zinc dextro tartrate crystals at different temperatures along with theoretical weight loss and experimental weight loss values

Sample	Temperature in °C	Weight in % (Theoretical)	Weight in % (experimental)
$Zn\ C_4\ H_4O_6\ 2H_2O$ (Levo-tartrate)	30	100	100
$Zn\ C_4\ H_4O_6$	120	85 56	84.22
ZnO_2	450	39 05	39
ZnO	800	32 63	32 97
$Zn\ C_4\ H_4O_6\ 2H_2O$ (Dextro-tartrate)	30	100	100
$Zn\ C_4\ H_4O_6$	130	85 56	84.74
ZnO_2	440	39 05	38 5
ZnO	800	32 63	32 89

In the present investigation three different equations, namely, the Coats-Redfern relation [13], the Horowitz-Metzger relation [14] and Freeman-Carroll relation [15], are applied to evaluate the kinetic parameters from the thermograms of Figures 1 and 2.

The Coats and Redfern relation [13] is described by the following equation

$$\log_{10}\left\{1-(1-\alpha)^{1-n}/T^2(1-n)\right\}$$

$$=\left\{\log 10[AR/aE][1-2RT/E]\right\}-\left\{E/2.3RT\right\}, \quad (1)$$

where E is the activation energy, A is the frequency factor, α is the fraction of decomposed material at time t, n is the order of reaction and T is the absolute temperature.

Horowitz and Metzger relation [14] is as follows :

$$\log_{10}\left[1-(C)^{1-n}/1-n\right]=E\theta/2.303\,RT_s^2\,, \quad (2)$$

where $\theta = T - T_s$ and T_s is chosen from the curve of decompose fraction *versus* time at maximum value of slope.

Freeman and Carroll relation [15] is given as follows

$$\left\{-E/2.3\,R\Delta(1/T)\right\}/\left\{\Delta\log W_r\right\}$$

$$=-x+\left[\left\{\Delta\log dw/dt\right\}/\left\{\Delta\log W_r\right\}\right], \quad (3)$$

where W is the total weight loss upto time t, W_c is the weight loss at the completion of the reaction and x is the order of reaction here, $W_r = W_c - W$.

The Coats and Redfern relation assumes the decomposition of substance in the following manner :

$$d\alpha/dt = k(1-\alpha)^n; \quad (4)$$

whereas, the Horowitz and Metzger relation assumes the decomposition as follows :

$$dC/dt = -k\,C^n, \quad (5)$$

where C is the concentration, mole fraction or amount of reactant.

Also, the Freeman and Carroll relation [15] suggests that the disappearance of the reactant is having the same nature as the Horowitz and Metzger relation. However all the three relations incorporate Arrhenius law in the analysis, but subsequent mathematical analysis and treatments are different, which leads to different equations. The Freeman and Carroll analysis uses the technique of differential thermal analysis, while Horowitz and Metzger relation incorporates an approximate integral method for the analysis.

These equations are applied to the first stage of the decomposition, *i.e.* dehydration of crystals. The detailed analysis

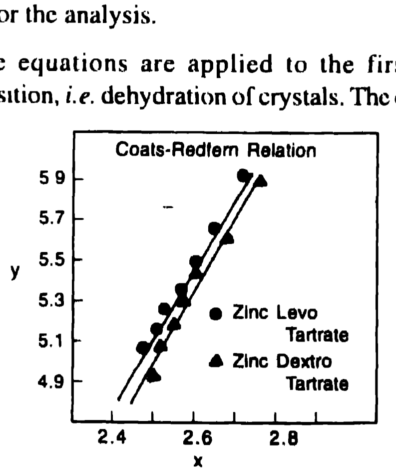

Figure 3. The plots for Coats-Redfern relation, where $Y = -\log[\{1-(1-\alpha)^{1-n}\}/T^2 \times (1-n)$ and $X = 1/T \times 10^3$ in K^{-1}

is discussed by Joseph and Joshi [16], elsewhere. Figure 3 indicates the plots for Coats-Redfern relation. the values of order of reaction, activation energy, and frequency factor are calculated. Using the values of frequency factor the values of entropy are estimated. Figure 4 shows the plots for Horowitz-

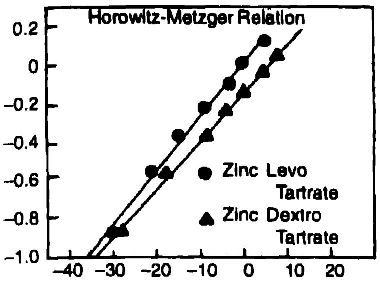

Figure 4. The plots for Horowitz-Metzger relation, where $Y = \log[(1-(1-\alpha)^{1-n})/(1-n)]$ and $X = \theta$.

Metzger relation, whereas Figure 5 exhibits plots for Freeman-Carroll relations, for both zinc levo and dextro tartrate crystals. The values of kinetic and thermodynamic parameters are

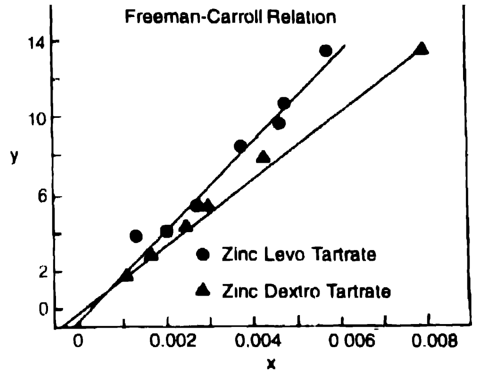

Figure 5. The plots for Freeman-Carroll relations, where $Y = (\Delta \log dw/dt)/(\Delta \log W_r)$ and $X = (\Delta T^{-1})/(\Delta \log W_r)$

calculated and listed in Table 2. It can be noticed from Table 2 that the order of reaction is ½ and ¼ for zinc levo tartrate and zinc dextro tratrate crystals, respectively, which remains constant for all the three relations. The values of activation energy and enthalpy of activation (ΔH) are high for zinc levo tartrate crystals than those of zinc dextro tartrate crystals for all the three relations. Also the difference in the values of activation energy for different equations is due to different kinds of mathematical models used.

Similar results were obtained in the case of copper levo tartrate and copper dextro tartrate crystals. The values of order of reaction, activation energy, entropy and Gibbs free energy were found to be greater in the case of copper levo tartrate then the crystals of copper dextro tartrate [1]. This difference is attributed to the different type of optically sensitive tartaric acids used to grow the crystals.

In conclusion, the values of activation energy and enthalpy of activation are high for zinc levo tartrate crystals then zinc dextro tartrate crystals, which may be due to different optically

Table 2. The values of different kinetic and thermodynamic parameters.

Sample	Order of reaction	Activation energy kJMol^{-1}	Frequency factor	Entropy JK^{-1}Mol^{-1}	Enthalpy of activation (ΔH) kJMol^{-1}
C–R Relation Levo tartrate	1/2	114 88	5 37 × 10^{25}	245.26	106 51
C–R Relation Dextro Tartrate	1/4	79 84	1 34 × 10^{21}	157.30	73 34
H–M Relation Levo tartrate	1/2	86 65	–	–	80 03
H–M Relation Dextro tartrate	1/4	73 18	–	–	66 68
F–C Relation Levo tartrate	1/2	39 61	–	–	32 99
F–C Relation Dextro tartrate	1/4	34 81	–	·	28 31

synsitive acids used to grow the crystals. The kinetic and thermodynamic parameters are found to be sensitive to the type of acids used to grow the crystals.

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